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(54) Title: FILLER COMPOSITION, METHOD OF PRODUCING FILLER COMPOSITION AND PAPER OR PAPERBOARD COMPRISING THE FILLER COMPOSITION

(57) Abstract: Filler composition for paper or paperboard in the form of an aqueous composition comprising particles of calcium carbonate and silica, wherein separate particles in the filler composition comprise a, preferably right through, amorphous mixture of calcium carbonate and silica. The filler composition is produced by reacting an alkali metal silicate solution, comprising particles of calcium hydroxide, with carbon dioxide.

FILLER COMPOSITION, METHOD OF PRODUCING FILLER COMPOSITION AND PAPER OR PAPERBOARD COMPRISING THE FILLER COMPOSITION

TECHNICAL FIELD

The invention relates to a new filler composition for paper or paperboard, in the form of a water-based composition comprising particles of calcium carbonate and silica. The invention also relates to a method for the preparation of the filler composition and to a paper or a paperboard comprising the filler composition according the invention.

BACKGROUND OF THE INVENTION

The greater part of all paper produced contains fillers in the form of mineral material. The original reason for use of fillers is economical as a more expensive fibre material can be replaced by a cheaper mineral material. In addition, many of the paper properties are ameliorated. Above all, improved printability properties are obtained by improving the surface smoothness, opacity and whiteness of the paper. The absorption of printing ink is higher and more even, the picture representation is improved and the paper gloss after calendering can be improved. As other advantages can be added a better dimensional stability, a better appearance and a better "sensation".

As mentioned above, the ability of the filler to increase the brightness of the finished paper is important. This results in a reduced or eliminated need to add expensive optical whitening agents if the filler has a high brightness. Calcium carbonate is the most frequently used conventional filler but other fillers are also used on a small scale, such as clay, titanium dioxide, talc and silicon dioxide (silica). Also organic fillers are described in the literature. Example of these are polymers of urea or formaldehyde.

Calcium carbonate exists in several forms when being used as a filler and the majority of fine papers contain calcium carbonate up to 25 % by weight. Ground marble, ground chalk and precipitated calcium carbonate are the most frequent types. The last mentioned type, precipitated calcium carbonate, is often called PCC, an abbreviation for the English term "Precipitated Calcium Carbonate". The use of PCC has increased in the last few years and today PCC is the dominant filler at production of fine paper in Sweden. A great number of patents have been published, describing production of PCC and its use as filler in paper, for example US. 5,332,564.

In the most common method of PCC production, the starting material is limestone which is heated up and then transformed to burned lime. The burned lime is allowed to react with water, thus forming calcium hydroxide. As carbon dioxide is then lead into the calcium hydroxide, calcium carbonate (PCC) is precipitated as a precipitation. Inter alia by choosing different temperature conditions during the last mentioned reaction, different shapes of the particles of PCC can be obtained, of which the scalenoedric and the rhombic shapes are the most frequent but also other shapes of particles exist in paper making.

Accordingly, as mentioned above, the ability of the filler to increase the opacity is very important. By an increased opacity the grammage of the paper can be reduced with great economic savings as a consequence. An increased opacity for a copy paper or a paper intended for offset printing also permits that both of the sides of the paper can be more effectively utilized for printing or copying without the print on one side being disturbed by the print on the opposite side. For a paper intended for e.g. envelopes the importance of a good opacity is great.

Of the fillers used today to increase the opacity, more than what is possible to achieve by use of calcium carbonate, titanium dioxide is the filler most frequently used. However, the use is strictly limited because of the high cost of titanium dioxide in combination with its poor filler retention. As the organic fillers are much more expensive than titanium dioxide, its even more unusual that such fillers are used.

In the literature there are furthermore a number of descriptions of how silica particles, which may be used in paper making, are formed by acidification of a silicate solution. In the literature and in patents these silica particles are denoted as i.a. poly silicic acid, silicic acid sols, silica sols, poly micro silicate gels, colloidal silica, colloidal silicon dioxide, active silica and silica micro gels.

The preparation of silica particles is described in the book "Soluble silicates" Volume II, by James G. Vail, published 1960. Silica particles can be produced in several different ways, one of these ways being acidification of aqueous solutions of alkali metal silicates by means of acids, acid salts or gases. The most frequent alkali metal silicate is sodium silicate solution, often called "water-glass" and examples of acidifying compounds, which can be used, are sulphuric acid, iron chloride and carbon dioxide. This method of producing silica particles, also described in several patents, EP 0 359 552 being one of them, may also be used for covering inorganic particles with

silica. This is described i.a. in US 5,340,393 and EP 0 941 964, specifying that also particles of calcium carbonate may be covered by a layer of silica. As these methods of producing particles of silica are relatively complicated and costly, they are not used commercially in any appreciable extent, if any.

Another important property of the paper which is influenced by the filler is its printability properties. In addition to the already mentioned properties, such as higher and more even absorption of printing ink and a better picture representation, being up to now important in above all offset printing, more and more effort has been put in on achieving better printability properties when utilizing so called ink jet printers. A paper which has good printability properties for ink jet printers is above all characterised in the following:

Minimal or none-existent ink spread outside the printed object so that the object does not receive uneven and straggly edges. The objects, for example letters if it is a text that is printed out, are perceived as indistinct and blurred if this property is not fulfilled. The ink spread is measured by visual methods or by an image analysis instrument.

High optical density. The property is most often measured by an optical densitometer.

Minimal print-through. This is not achieved if too strong a penetration of the pigments or the dyes of the ink into the paper has the result that the colour appears on the back of the paper. A high print-through often results in a low optical density. The print-through is measured visually or by an optical densitometer.

Low or non-existent so called bleeding. If ink is supplied to a surface where ink in another colour already has been applied, one colour may flow into the other colour. This problem, caused by too slow penetration into the paper, is called bleeding and is measured visually or by a densitometer.

To achieve a paper with good printability properties for ink jet printers, the known technology has up to now offered special, very expensive, pigments and by using PCC satisfying properties have not been achieved to this end, up to now.

DISCLOSURE OF THE INVENTION

The object of the invention is to offer a new and improved filler composition, by which the problems mentioned above are eliminated or restricted and/or great economical profits are achieved.

Its another object of the invention to provide a new filler composition which gives the paper a higher opacity in a much more cost effective way than known compositions.

Yet another object of the invention is to provide a new and improved filler composition which gives the paper higher brightness and/or can reduce the need of optical whitening agents.

Another object of the invention is to provide a new filler composition which improves the printability properties of the paper when using ink jet printer.

Another object of the invention is to provide a paper with improved properties.

According to the invention these and other objects are achieved by providing a filler composition for paper or paperboard in the form of an aqueous composition comprising particles of calcium carbonate and silica where separate particles in the filler composition comprise a, preferably right through, amorphous mixture of calcium carbonate and silica. Further more, according to the invention, this filler composition has been produced by reacting a solution of alkali metal silicate, which comprises particles of calcium hydroxide, with carbon dioxide.

It has surprisingly been found that by using the above mentioned composition, effects are obtained that considerably reduce or eliminate a lot of the shortcomings, which may be attributed to the prior art. Inter alia, the printability properties, brightness and opacity of the paper are improved. More specifically the printability properties of the paper are improved in connection with the use of ink jet printers whereby the ink spread decreases, the optical density increases, the print-through decreases and the bleeding decreases or is eliminated.

A theory is that the positive, surprising effects of the invention may be dependent on that the separate particles of the filler composition consist of a, preferably right through, amorphous combination/mixture of silica and calcium carbonate, which i.a. has the consequence that the filler composition exhibits a considerably higher specific surface

than precipitated calcium carbonate or a filler composition produced according to US 5,340,393 where silica only covers a nucleus of solely calcium carbonate, formed in an earlier step. Another difference, as compared to US 5,340,393, is that it there is used mineral acid as acidification agent.

The high specific surface of the filler according to the invention contributes to its high refractive index, determining the opacity increasing ability of the filler. The high specific surface of the filler composition is probably also the reason for the improved printability properties in connection with the use of ink jet printers as the ink absorption of the paper is improved due to an increased number of capillaries having smaller radius.

According to one specific embodiment of the invention, the method of producing the filler composition according to the invention may on the whole be the same as is described in US 5,332,654, the difference being that the sludge of calcium hydroxide also comprises alkali metal silicate. According to the invention, quick lime is slaked to calcium hydroxide in a aqueous solution comprising sugar. To the formed sludge, alkali metal silicate is added and after that a gas containing carbon dioxide is brought to bubble through the sludge, preferably under stirring, until pH decreases to a pH of about 6-9, preferably 7-8 for carbonation during formation of amorphous particles having a high specific surface and consisting right through of mixed calcium carbonate and silica. The silica to calcium carbonate ratio in the produced particles is preferably 1:100 - 20:100.

Also other parameters for the method according to the invention may be in accordance with US 5,332,654, the content of which is incorporated herein by reference.

The shape of the produced particles of calcium carbonate and silica can be varied by choice of reaction temperature.

The amount of sugar which is utilized may be approximately 0.1-2 % by weight, preferably 0.1-0.3 % by weight, calculated on the weight of calcium carbonate plus silica which is to be produced. The sugar preferably consists of a mono- or disaccharide, more preferably sucrose. The function of the sugar in this connection is that it gives the calcium hydroxide a slightly greater specific surface and that it influences the solubility of the calcium hydroxide. It may also be the case that the sugar not is needed in connection with the invention, as silica may have the same effect as sugar.

According one aspect of the invention the carbon dioxide containing gas carbon dioxide is constituted by a flue gas or a gas comprising carbon dioxide extracted from flue gas, the content of carbon dioxide in the carbon dioxide containing gas being 5-100 %. Alternatively the carbon dioxide may be added in the form of carbon dioxide in a liquid.

EXAMPLE 1

To a sludge of calcium hydroxide of 15 % by weight which also contains a sugar solution of a concentration of 0.15 %, a sodium silicate solution was added with a SiO_2/Na_2O ratio of 3.35 (molar ratio), 28.2 % by weight SiO_2 and 8.7 % by weight Na_2O so that the ratio $Ca(OH)_2$ to SiO_2 was 8:1. The temperature of the mixture was initially 35°C. To this mixture of high pH value, carbon dioxide gas was added until a pH of approximately 7.5 was obtained. The composition thus obtained was added to a fine paper stock whereby a filler content of 22 % by weight was obtained.

The paper produced from this stock exhibited considerable improvements in terms of opacity, brightness and printability properties for ink jet printers as compared to a paper produced with 22 % by weight PCC produced without addition of sodium silicate solution.

EXAMPLE 2

For the purpose of comparing the invention with a concept developed further from US 5,340,393, carbon dioxide was added to a sludge of calcium hydroxide also containing a sugar solution of 0.15 %, so that the pH value was reduced to approximately 7.5. To the sludge of precipitated calcium carbonate thus prepared, a sodium silicate solution of the same type as in Example 1 was dosed, whereby the calcium carbonate to silica ratio became 15:1, causing the pH value to rise again. The temperature of the mixture was initially 35 °C. Carbon dioxide was added to this mixture so that the pH once again was reduced to approximately 7.5. This filler composition too was added to a paper stock whereby a filler content of 22 % by weight was obtained.

The paper produced from this stock showed no improvements in terms of opacity, brightness and printability properties for ink jet printers as compared to a paper produced with 22 % by weight PCC produced without addition of solution of sodium silicate.

CLAIMS

1. Filler composition for paper or paperboard in the form of an aqueous composition comprising particles of calcium carbonate and silica, characterised in that separate particles in the filler composition comprise a, preferably right through, amorphous mixture of calcium carbonate and silica.

2. Filler composition for paper or paperboard in the form of an aqueous composition comprising particles of calcium carbonate and silica, characterised in that it has been produced by reacting an alkali metal silicate solution, comprising particles of calcium hydroxide, with carbon dioxide.

3. Filler composition as claimed in claim 1 or 2, characterised in that the silica to calcium carbonate ratio in the particles is 1:100 - 20:100.

4. Method of producing a filler composition for paper or paperboard in the form of an aqueous composition comprising particles of calcium carbonate and silica, characterised in that an alkali metal silicate solution, comprising particles of calcium hydroxide, is brought to react with carbon dioxide.

5. Method according to claim 4, characterised in that said reaction with carbon dioxide is brought to a pH of 6-9, preferably 7-8 in the solution.

6. Method according to any one of claims 4-5, characterised in that the calcium hydroxide containing alkali metal silicate solution is brought in contact with the carbon dioxide by a carbon dioxide containing gas being brought to bubble through the calcium hydroxide containing alkali metal silicate solution, or by mixing a carbon dioxide containing liquid with the calcium hydroxide containing alkali metal silicate solution.

7. Method according to claim 6, characterised in that said carbon dioxide containing gas contains carbon dioxide in an amount of 5-100 % by weight, the gas preferably being constituted of a flue gas or a gas comprising carbon dioxide extracted from flue gas.

8. Paper or paperboard, characterised in that it comprises a filler composition according to any one of claims 1-3, or a filler composition produced by the method according to any one of claims 4-7.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 00/02388

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 17/69, C09C 1/02, C09C 1/30
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21H, C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5340393 A (JACOBSON), 23 August 1994 (23.08.94), abstract ---	1-8
A	US 3373134 A (EIZO YASUI, ET AL), 13 August 1964 (13.08.64), column 2, line 35 - line 42 ---	1-8
A	US 5332564 A (CHAPNERKAR, ET AL), 26 July 1994 (26.07.94), abstract --- --------	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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INTERNATIONAL SEARCH REPORT

Information on patent family members

05/02/01

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5340393 A	23/08/94	AU 4288093 A	29/11/93
		DE 69321228 D,T	18/03/99
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		DE 1592972 A	11/02/71
		FR 1458935 A	27/01/67
US 5332564 A	26/07/94	NONE	